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14. ABSTRACT The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.						
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POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #9

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1 Summary

Having observed self-healing in real time using electrochemical impedance spectroscopy, we now show through this same technique the importance of the microcapsules in extending the lifetime of the Zn rich coating. Initial thermogravimetric analysis (TGA) data from our humidity exposure testing suggests that the OTS rich microcapsules have an improved shelf-life in comparison to polyurethane resin-filled microcapsules. Salt spray measurements, now completed, show our self-healing coatings containing microcapsules rich in Octadecyltrimethoxy silane (OTS) exhibit corrosion prevention comparable to zinc-filled primers. PPG's continued examination of the coatings with respect to shelf life, adhesion, metal coating, and shear stress will help further refine Polyfibroblast design changes proposed for FY12.

2 Project Goals and Objectives

The only milestone remaining was to show that microcapsules can withstand one week at 100°F and 100% relative humidity without losing liquid. Initial thermogravimetric analysis (TGA) data from our humidity exposure tests suggests that while our original polyurethane resin-filled microcapsules are not able to withstand these conditions, microcapsules rich in Octadecyltrimethoxy silane (OTS) may meet these criteria.

3 Key Accomplishments

3.1 Direct Electrochemical Measurement of Self-Healing

Our test coatings contain a constant total volume of “additives” – Zn powder and polyfibroblast microcapsules; as such, we want to know the optimal ratio of Zn:Microcapsules that will give the best corrosion protection. Preliminary electrochemical measurements suggest that coatings containing 50% Zn provide better corrosion protection than coatings containing higher amounts of zinc (95%).

Steel panels were prepared for testing with the following formulations: 1) Polyfibroblast microcapsules containing 25% MPTMS, methylpropyltrimethoxy silane, combined with Zn powder (50:50 w/w) in MIL-P resin; and, 2) Polyfibroblast microcapsules containing 5% ITS, isocyanatoethyltrimethoxy silane combined with Zn powder (5:95 w/w) in MIL-P resin. For impedance testing, panels were independently immersed in an aqueous solution of 1%wt. each of the sodium salts of carbonate, chloride and sulfate – the standard solution for the ASTM G42 coating delamination test – with the impedance continuously monitored. An incision was made in the coatings once the impedance reached a steady state value, suggesting equilibrium between the coating and the electrolyte. The impedance was continuously monitored for several additional hours, until reaching a steady state, when the coating was assumed to be fully resealed and cured.

The linear polarization (LP) technique was performed only after the post-incision coating impedance reached a steady state value. Linear polarization (LP) is a corrosion measurement technique that details the corrosion rate by monitoring the current during the corrosion reaction.

It also provides information on the dc polarization resistance of the coating. Note that LP is a semi-destructive technique, and performing it before the coating is resealed could force the substrate to oxidize, generate iron oxide, and the volume change within the incision could impede with the curing process.

25% MPTMS with 50% Zn: Figure 1 shows the impedance and the LP data. The high frequency (>1 kHz) shows that the coating, before the incision, had a high impedance that was commensurate with “good” coatings. The low frequency (≤ 1 Hz) impedance was also high, about $2\text{ M}\Omega$, which is normal behavior for “good” coatings in contact with salt solutions. Upon incision, the impedance dropped by an order of magnitude due to the penetration of the electrolyte; however, it increased by a factor of 5 after 17 hours. The 5x increase is not normal for coatings without self-healing capability; therefore we attribute the increase to the action of the microcapsules.

The linear polarization data shows that the dc resistance of the self-healed coating is about $3\text{ M}\Omega$, and its corrosion current is about 9 nA . These values are quite typical of well coated steel exhibiting good corrosion resistance. Optical microscopy of the incision showed self-healed coating with little evidence of corrosion.

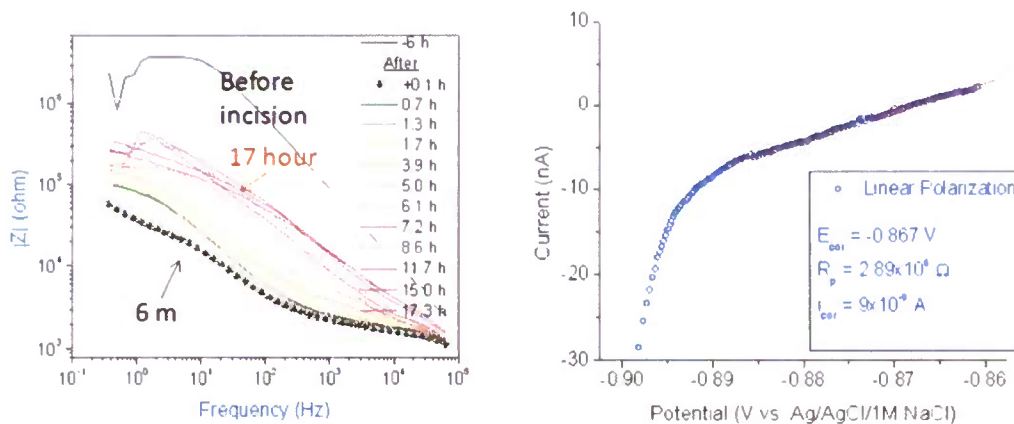


Figure 1: Left: Impedance data on a 15cm^2 25% MPTMS with 50% Zn in ASTM G42 solution at room temperature. The low frequency ($\leq 1\text{Hz}$) impedance is well above $2\text{ M}\Omega$ before the incision. The incision caused the impedance to drop well below $0.1\text{ M}\Omega$ that gradually increased to $0.5\text{ M}\Omega$ over a period of 17 hours. Right: the dc polarization resistance measured 17 hours after the incision was $2.89\text{ M}\Omega$, and the corrosion current was 9 nA .

5% ITS with 95% Zn: Figure 2 shows the impedance and the LP data. The high frequency (>1 kHz) shows that the coating, before the incision, had a high impedance, also representative of a good coatings. The low frequency (≤ 1 Hz) impedance was also high, about $2\text{ M}\Omega$, which is also normal behavior for a good coating. Incision caused the impedance to drop by an order of magnitude due to the penetration of the electrolyte; however, it recovered only back to $<0.1\text{ M}\Omega$, suggesting a recovery or resealed, but not as much as we observed in the MPTMS case (Figure 1 data) that contained 50% microcapsule.

The linear polarization data shows that the dc resistance of the self-healed coating is about $0.5\text{ M}\Omega$, and its corrosion current is about 55 nA . These values also indicate poor corrosion resistance; the substrate was corroding at rate that was one-order-of-magnitude higher than the MPTMS with 50% microcapsule. Optical microscopy of the incision showed evidence of corrosion products underneath the self-healed coating.

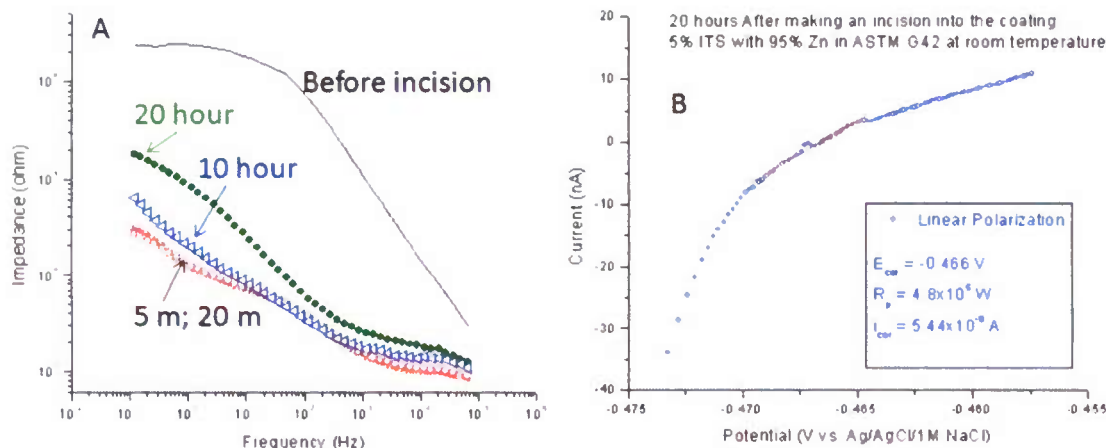


Figure 2: Left: Impedance data on a 15cm^2 5% ITS with 95% Zn in ASTM G42 solution at room temperature. The low frequency ($\leq 1\text{Hz}$) impedance is well above $2\text{ M}\Omega$ before the incision. The incision caused the impedance to drop well below $0.03\text{ M}\Omega$ that gradually increased to $0.1\text{ M}\Omega$ over a period of 20 hours. Right: the dc polarization resistance measured 20 hours after the incision was $0.5\text{ M}\Omega$, and the corrosion current was 55 nA .

3.2 Shelf Life

We repeated the shelf life tests for exposure to high humidity with a fresh sample of our “best practice” microcapsules prepared with careful control of plating conditions to see if we could improve the ability to protect the isocyanate monomer. In addition, we prepared a fresh sample of 50% OTS microcapsules using the same plating conditions. We then placed 500 mg of both microcapsule samples in a humidity chamber at 100°F for one week. The relative humidity was maintained at a constant level of 92.9% using a saturated potassium phosphate solution. Thermogravimetric analysis (TGA) measurements were obtained at Day 0 and again at Day 7.

Comparison of the phase plateaus shown in Figure 3 – the liquid plateau is around 240°C and the solid polymer plateau is around 350°C – suggest that more liquid is present in the 50% OTS microcapsules after 7 days in the humidity chamber. This is not surprising given that the OTS is not as prone to moisture-induced polymerization as diisocyanates.

Improvements in the processing of the OTS microcapsules may help to further extend the shelf life.

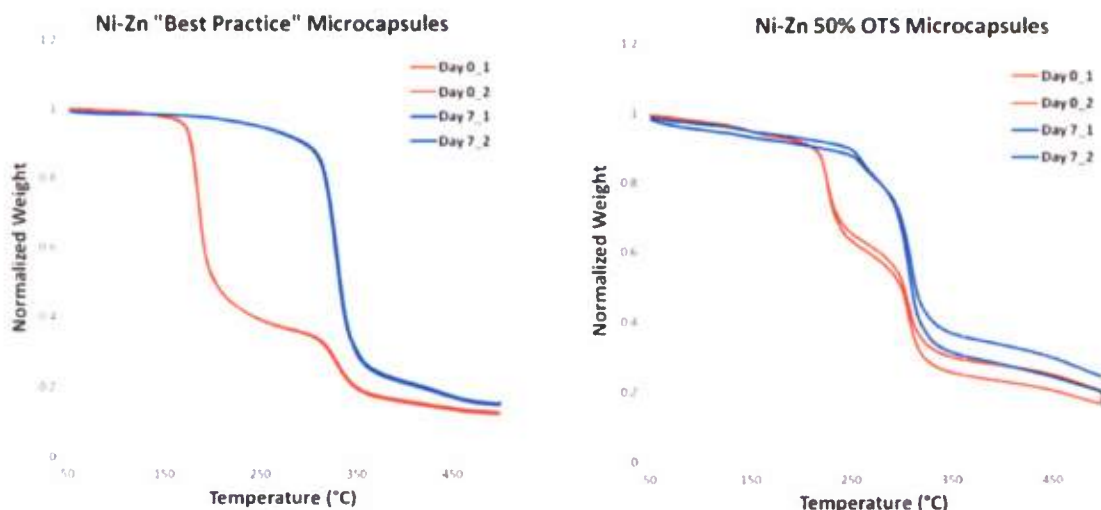


Figure 3: TGA data of our “best practice” polyurethane resin microcapsules vs. 50% OTS microcapsules at Day 0 and after 7 days in the humidity chamber.

3.3 Salt Spray Measurements

Salt spray measurements on the samples listed in Table 1 continued during this reporting period. The coatings were evaluated for their corrosion protection capabilities. Recall that the microcapsules were filled primarily with isophorone diisocyanate (IPDI), with a varying fraction of silane adhesion promoter. The silanes tested included methacryloxypropyltrimethoxy silane (MPTMS), octadecyltrimethoxysilane (OTS), and isocyanatotrimethoxysilane (ITS). Zinc-rich MIL-P-26915 primer served as the control.

After 1000 hours of exposure, the microcapsules filled with 80% OTS continued to outperform all other samples, including the, the MIL-P-26915 control sample.

Table 1: Sample List for Salt Spray Measurements

Panels	Percent Silane in Microcapsule Formulation
1B	10% MPTMS
1C	10% MPTMS
2B	20% MPTMS
2C	20% MPTMS
3B	20% OTS
3C	20% OTS
4B	80% OTS
4C	80% OTS
5B	10% ITS
5C	10% ITS
1	MIL-P-Resin w/ZINC

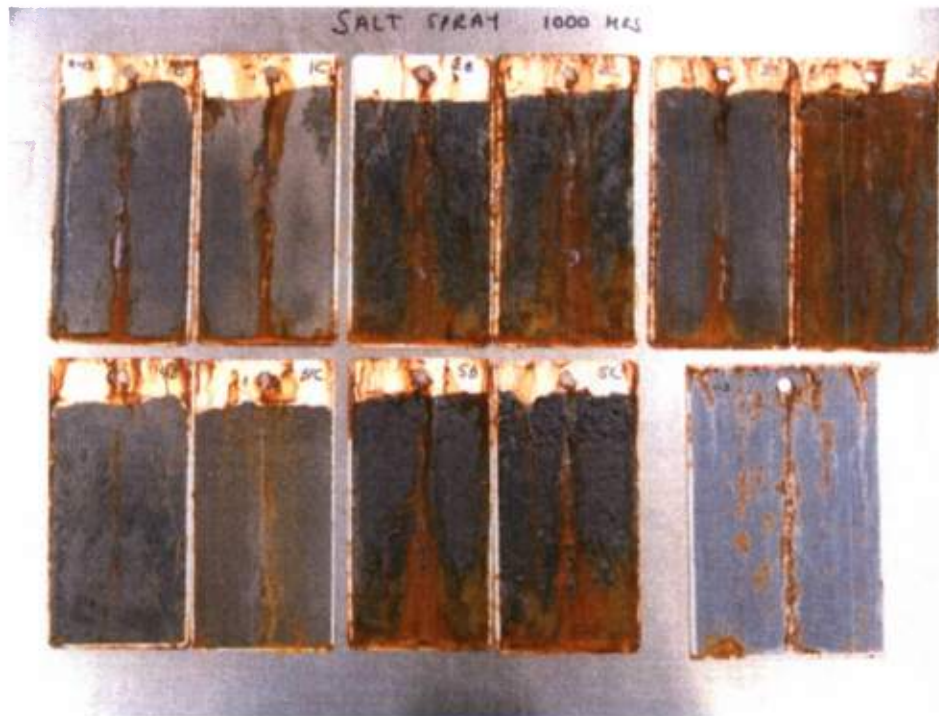


Figure 4: Salt spray panels after 1,000 hours exposure. Panels 4B and 4C, which were 80% OTS silane exhibit comparable corrosion protection to the zinc-rich MIL-P-26915.



Figure 5: Salt spray panels after 1,000 hours of exposure crosshatched to examine the scribe corrosion. The 80% OTS panels (4C) show no pitting at the along the scribe, comparable to the MIL-P-26915 control.

3.4 Paint Stability Testing

We reported initial results of PPG's shelf life tests last month. These hot room experiments consist of placing samples at 125°F for one week – a standard test to simulate the elevated temperatures encountered by paints during shipping. The initial results showed that the viscosity of polyurethane resin increased 4-fold with or without microcapsules, but that the doubling of viscosity for the filled epoxy resin was not observed for the unfilled epoxy resin.

Further hot room stability tests were conducted with the MIL-P resin and the Epoxy/amine resin using a 25% microcapsule loading. After 1 week in the hot room, the viscosity of both formulations increased, though neither completely cured. Free film samples were obtained by drawing the formulations on Tedlar® curing at room temperature for 7 days. The films were then cross sectioned and examined via SEM. The SEMs of the cross sections detected a small amount of liquid released along the cut; however, TGA of the films did not show the presence of liquid.

3.5 Adhesion of Spray Coatings with Microcapsules

Dried microcapsules were successfully incorporated into MIL-P resin at 10%, 25% and 40% loading levels and sprayed over 2 mil profile steel substrates. Optical microscopy of the coatings showed no significant microcapsule breakage. The panels were cured at room temperature for 7 days. Initial adhesion and appearance were good for all 3 formulations (Figure 6)



Figure 6: Mil-P resin with 10% microcapsules, before (left) and after (right) scratch.

The same experiment was performed using Zn rich primer in a 1:1 weight ratio with the dried microcapsules at 10%, 25% and 40% loading levels. These formulations were successfully mixed and sprayed over 2 mil profile steel substrates. Optical microscopy of the coatings showed no significant microcapsule breakage and the initial adhesion and appearance were good after the panels were cured at room temperature for 7 days.

3.6 Controlling Metal Composition

PPG examined the metal composition of different batches of microcapsules by ICP to determine the effects on metal composition of varying concentrations of Sn and/or Pd in the catalysis steps. Analysis of the results indicated that extra tin deposited on the capsules inhibits Ni deposition (Figure 7). Excess palladium on the microcapsules did not affect the plating.

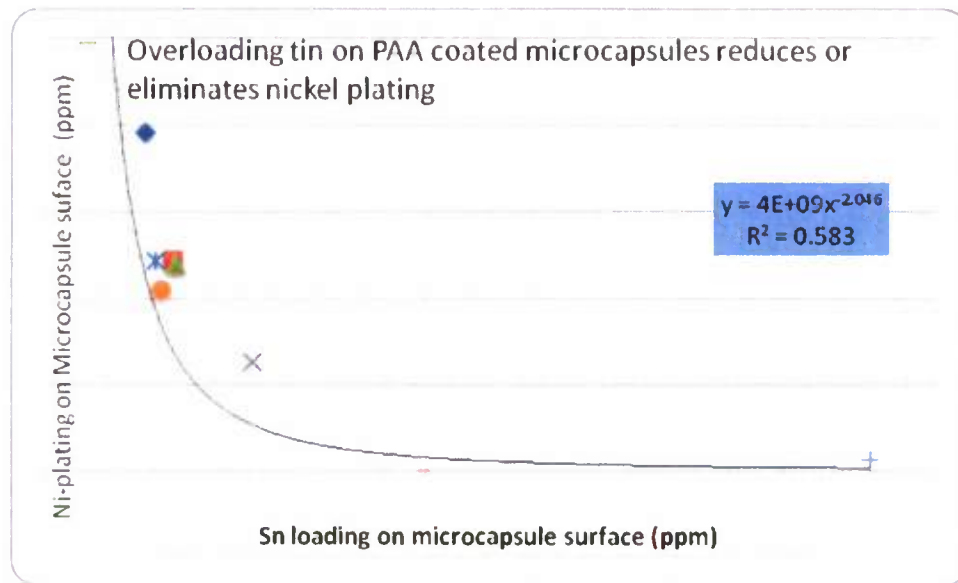


Figure 7: Effects of Sn loading on the microcapsule surface suggest that too high a loading inhibits Ni deposition.

3.7 Shear Stress Testing

PPG performed initial stress tests on formulations containing 10% and 34% microcapsule loading in MIL-P. Initial results showed that at speed up to 1000 rpm there is no significant breakage of the microcapsules. Good dispersions were obtained with 5-10 minute mixing.